## Electronic Supporting Information (ESI<sup>†</sup>)

# Metal organic framework devised Co-N doped carbon microsphere/ nanofiber hybrids as free-standing 3D oxygen catalysts

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### **Experimental Section**

**Materials**: Polyacrylonitrile (PAN) and Nafion (5 wt %) were purchased from Sigma–Aldrich. Carbon-supported Pt catalyst (20 wt %, Pt/C) was bought form Johnson Matthey. 2-Methylimidazole was got from Aladdin. Cobaltous nitrate (Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O), N,N-dimethylformamide (DMF), and methanol were purchased from Beijing Chemical Reagent Company (Beijing, China). All chemicals were analytical grade and used as received. All aqueous solutions were prepared with ultrapure water from a Water Purifier System (Sichuan Water Purifier Co. Ltd., China).

**Apparatus**: Scanning electron microscopy (SEM) images were obtained from an XL 30 ESEM FEG SEM (Philips, Netherlands). X-Ray diffraction data were got with model D8 ADVANCE (BRUKER, Cu K $\alpha$  radiation,  $\lambda$  =1.5406 Å). Transmission electron microscopy (TEM) images were measured with a JEM-2100F high-resolution transmission electron microscope (JEOL Ltd., Japan). X-ray photoelectron spectroscopy (XPS) and ultraviolet photoelectron spectroscopy (UPS) were performed using Thermo ESCALAB 250 (Thermo Scientific, USA). For the XPS analysis, monochromatic Al K $_{\alpha}$  (h $\gamma$  = 1486.6 eV) excitation was employed. For the UPS analysis, a He lamp was used with 21.2 eV (He(I)) excitation energies. Nitrogen sorption isotherms were obtained with an ASAP 2020 Physisorption Analyzer (Micrometrics Instrument Corporation). Electrochemical impedance spectroscopy (EIS) measurements were performed by a Zennium electrochemical workstation (Zahner, Germany). Surface-enhanced Raman scattering (SERS) spectra were measured with a Renishaw 2000 model confocal microscopy Raman spectrometer with a CCD detector and a holographic notch filter (Renishaw Ltd., Gloucestershire, U.K.). X-ray absorption fine structure (XAFS) spectroscopy was carried out at 1W2B end station, Beijing Synchrotron Radiation Facility

(BSRF). The Co K-edge spectra were recorded at room temperature in transmission mode. The electrochemical experiments were employed using a CHI842B electrochemical workstation (CH Instruments, Shanghai). Rotating ring-disk electrode (RRDE) techniques were performed on a Model RRDE-3A Apparatus (ALS, Japan) with CHI842B electrochemical workstation. The electrochemical experiments were performed through a three electrode system with a modified glassy carbon electrode (GCE) as the working electrode, an Ag/AgCl (saturated KCl) electrode as the reference electrode, and counter electrode (platinum foil), respectively. The potential, measured against an Ag/AgCl reference electrode, was converted to the E versus the reversible hydrogen electrode (RHE) according to E(vs RHE) = E(vs Ag/AgCl) + 0.059pH + 0.197. All the electrochemical measurements were carried out at room temperature.

#### Synthesis of the composites

Firstly, ZIF-67 was synthesized by the reported method from  $Co(NO_3)_2 \cdot 6H_2O$  and 2methylimidazole. And then, 2.4 g of ZIF-67 was dissolved into 5.0 mL of DMF and ultrasonic 0.5 h. And then, 0.3 g of PAN was added into the above solution and stirred for 12 h. The precursor was filled into a plastic syringe with 7-gauge needle which was connected to a High Voltage DC Power Supply (Dongwen, Tianjin). A constant volume flow rate was maintained via a syringe pump (KDS 100, KD–Scientific). The aluminum foil was used as a collector. The applied voltage was 20 kV, the distance between the nozzle tip and the collector was 18 cm, and the flow rate was 2.0 mL/h. Thereafter, heat treatments were carried out with the electrospun nanofibers at 200 °C for 12 h in a drying oven. The remaining product was heated at 240 and 800 °C for 2 and 1 h, respectively, with a heating rate of 2 °C/min in N<sub>2</sub>.

For simplicity, the resulting samples were named as ZP(x:y)-T according to the ratio of ZIF-67 to PAN (x:y), as well as the pyrolysis temperature (T °C). For comparison, ZIF-67 and PAN were also pyrolysed at 800°C under the same conditions and named as ZP(1:0)-800 and ZP(0:1)-800, respectively.

#### Electrocatalytic activity evaluation.

The GCE was polished carefully with 0.3  $\mu$ m alumina slurries, followed by sonication in acetone, ethanol, and ultrapure H<sub>2</sub>O successively, and then dried at room temperature. The catalyst was cut by punching with suitable diameter and then glued on the surface of GCE by 0.2% Nafion and dried under an infrared lamp.

Meanwhile, the ORR was performed in O<sub>2</sub>-saturated 0.50 M H<sub>2</sub>SO<sub>4</sub> and 0.10 M KOH at a rate of 50

mV s<sup>-1</sup> from 0.212 to 1.012 V and 1.164 to 0.364 V, separately. Before experiments, all the electrodes were activated by potential cycling in 0.50 M  $H_2SO_4$  or 0.10 M KOH at a scan rate of 50 mV s<sup>-1</sup>.

For RRDE and RDE experiments, the ORR polarization curves were obtained by performing a negative-direction sweep of potential at a scan rate of 5 mV s<sup>-1</sup> from 0.212 to 1.012 V and 1.164 to 0.164 V (vs RHE) in O<sub>2</sub>-saturated 0.50 M H<sub>2</sub>SO<sub>4</sub> and 0.10 M KOH. The ring potential was set 1.012 or 1.264 V in 0.50 M H<sub>2</sub>SO<sub>4</sub> and 0.10 M KOH, respectively. Instead, 0.10 M HClO<sub>4</sub> was used for the Pt/C modified GCE under the same conditions.



Fig. S1 TEM images of (a) as-produced ZIF-67 and (b) ZP(1:0)-800 materials.



Fig. S2 SEM images of as-electrospun ZP(8:1) hybrid with different magnifications.



Fig. S3 SEM images of the (a) ZP(8:1)-700 and (b) ZP(8:1)-900. TEM images of the (c) ZP(8:1)-700 and (d) ZP(8:1)-900.



Fig. S4 SEM MAP DATA of the ZP(8:1)-800.



Fig. S5 Pore distribution of ZP(8:1)-800 and ZP(1:0)-800.



Fig. S6 TGA of ZP(8:1)-800.



**Fig. S7** XPS of the ZP(8:1)-800.



Fig. S8 XPS C1s of the ZP(8:1)-800.



Fig. S9 (a) Raman and (b) EIS of different samples, (c) CVs of the ZP(8:1)-800 electrode in 0.50 M H<sub>2</sub>SO<sub>4</sub>, (d) Plots of ΔJ vs scan rate of different samples at 0.312 V in 0.50 M H<sub>2</sub>SO<sub>4</sub>, (e) Water contact angle of the surface of ZP(8:1)-800, (f) UPS spectra of different samples.



Fig. S10 CVs of the (a) ZP(0:1)-800, (b) ZP(1:3)-800, (c) ZP(3:1)-800 and (d) ZP(1:0)-800.



Fig. S11 Water contact angle of the (a) ZP(0:1)-800, (b) ZP(1:3)-800, (c) ZP(1:1)-800 and (d) ZP(6:1)-



**Fig. S12** SEM of the (a) ZP(0:1)-800, (b) ZP(1:10)-800, (c) ZP(1:8)-800 and (d) ZP(1:6)-800, (E) ZP(1:4)-800, (F) ZP(1:3)-800, (g) ZP(1:1)-800, (h) ZP(2:1)-800 and (i) ZP(3:1)-800.



Fig. S13 SEM of the (a) ZP(4:1)-800, (b) ZP(6:1)-800, (c) ZP(7:1)-800 and (d) ZP(8:1)-800.



Fig. S14 SEM of the ZP(8:1)-800 with different electrospinning fluid rate: (a) 0.5, (b) 1.0, (c) 1.5, and (d) 2.0 ml/h.



Fig. S15 Illustration of the growth mechanism of the CSFHs.



Fig. S16 RRDE of different materials from different ratios of ZIF-67 to PAN (x:y) in  $O_2$  -0.5 M  $H_2SO_4$ .



Fig. S17 H<sub>2</sub>O<sub>2</sub> and n of commercial Pt/C in 0.10 M HClO<sub>4</sub> solution.



Fig. S18 LSV of commercial Pt/C after 3000 CV cycles in 0.10 M HClO<sub>4</sub>.



Fig. S19 CVs of (a) ZP(8:1)-800 and (b) commercial Pt/C samples with and without 1.0 M methanol in  $0.50 \text{ M H}_2\text{SO}_4$  (Pt/C in  $0.10 \text{ M HClO}_4$ ).



Fig. S20 (a) LSV of ZP(8:1)-800 for ORR with or without 50 mM SCN<sup>-</sup> in 0.50 M H<sub>2</sub>SO<sub>4</sub>. (b) i-t curves of ZP(8:1)-800 for ORR with addition of SCN<sup>-</sup>.



Fig. S21 H<sub>2</sub>O<sub>2</sub>% and n of (a) ZP(8:1)-800 and (b) commercial Pt/C samples in 0.10 M KOH. LSV of (c) ZP(8:1)-800 and (d) commercial Pt/C after 3000 CV cycles in 0.10 M KOH.



Fig. S22 LSV for OER of commercial RuO<sub>2</sub> and ZP(8:1)-800 in 0.10 M KOH.

**Table S1** Comparisons of ORR performances for ZP(8:1)-800 with other non-precious metal carbon (NPMC) electrocatalysts in acidic solution.

Materials	E <sup>a</sup> <sub>1/2</sub> (vs. RHE)	E <sup>a</sup> onset(vs. RHE)	BET area	References
N-G-CNT	~0.51	-	$155m^2g^{-1}$	[1]
NT-G	0.76	0.89		[2]
Fe-N-C/CNTs	0.67	0.83	$540 \text{ m}^2 \text{ g}^{-1}$	[3]
FeIM/ZIF-8	0.755	0.915	572 m <sup>2</sup> g <sup>-1</sup>	[4]
Fe <sub>3</sub> C/C-700	0.73	0.9		[5]
CoP-CMP	0.64	0.74	$480 \text{ m}^2\text{g}^{-1}$	[6]
PpPD-Fe-C	0.718	0.826		[7]
Fe–AAPyr	0.75	0.9		[8]
Fe/N/C	~0.72	0.92	$598 \text{ m}^2\text{g}^{-1}$	[9]
PI–Fe–C	0.78	0.92	$624 \ m^2 g^{-1}$	[10]
Co/NS-CNT-600	~0.42	~0.7		[11]
Co@NG-acid	0.63	0.77		[12]
Co-N-C	0.761	-	$484 \text{ m}^2\text{g}^{-1}$	[13]
NCNFs/acid/NH <sub>3</sub>	~0.592	0.812		[14]
ZIF/rGO-700-AL	~0.72	0.92	$512 \text{ m}^2\text{g}^{-1}$	[15]
Zn-ZIF/GO-800	~0.68	0.85	$1170 \text{ m}^2\text{g}^{-1}$	[16]
FP-Fe-TA-N-850	~0.6	0.83		[17]
Co-N/HGS	0.53	0.65	$321 \text{ m}^2\text{g}^{-1}$	[18]
ZP(8:1)-800	0.794	0.845	$364 m^2 g^{-1}$	This work

N-G-CNT: nitrogen-doped graphene/CNT composite
NT-G: few-walled (two to three walls) carbon nanotube–graphene
FeIM: [Fe<sub>3</sub>(imid)<sub>6</sub>(imidH)<sub>2</sub>]x
CoP-CMP: cobalt porphyrin-based conjugated mesoporous polymer
PpPD: polymerized o,m,p-phenylenediamine
AAPyr: 4-aminoantipyrine
PI: polyimide
Co/NS-CNT-600: Co supported on nitrogen and sulfur co-doped vertically-aligned carbon nanotubes
FP-Fe-TA-N-850: Filter paper-Fe- Tannic acid
Co–N/HGS: cobalt–nitrogen-doped hollow graphene sphere

**Table S2** Comparisons of ORR performances for ZP(8:1)-800 with other NPMC electrocatalysts in basic solution.

Catalysts	E <sup>a</sup> 1/2(vs. RHE)	E <sup>a</sup> onset(vs. RHE)	<b>BET</b> area	References
Fe-derived NCNT	0.89	0.71	870	[19]
pPMF	0.973	0.879	190	[20]
G/CNT/Co	0.95	0.86	-	[21]
BCN-FNHs	-	0.861	151.2	[22]
Co@N-CNTs-m	0.929	0.849	-	[23]
Co-C@NWCs	0.939	0.83	121.6	[24]
Co@Co <sub>3</sub> O <sub>4</sub> @PPD	~0.864	~0.794	-	[25]
HDPC	0.95	0.79	345.7	[26]
Fe <sub>x</sub> Co <sub>(1-x)</sub> -N/PC		0.812	634.3	[27]
Co-MOF@CNTs (5	0.91	0.82	-	[28]
wt%)				
CoO@N/S-CNF	0.84	0.722	129	[29]
Co-N-C		0.8	226	[30]
Co/NC		0.83	233	[31]
Co <sub>3</sub> O <sub>4</sub> /NRGO	0.92	0.83	-	[32]
C@Co-NGR	0.910	0.830	342.2	[33]
ZP (8:1)-800	0.96	0.878	364 m <sup>2</sup> g <sup>-1</sup>	This work

 $E^b\!\!:$  potential in basic solution;  $E^a\!\!:$  potential in acidic solution

**pPMF**: porous bamboo-like carbon nanotube/Fe<sub>3</sub>C nanoparticles

BCN-FNHs: bamboo-like carbon nanotube (b-CNT)/Fe<sub>3</sub>C nanoparticle (NP) hybrids

Co@N-CNTs-m: Co nanoparticle-encapsulated N-doped carbon nanotube

HDPC: heteroatom (N, P, Fe) ternary-doped, porous carbons

FeNi@NC: single layer graphene encapsulating FeNi

Co<sub>3</sub>O<sub>4</sub>C-NA: Co<sub>3</sub>O<sub>4</sub>-carbon porous nanowire arrays

Co<sub>3</sub>O<sub>4</sub>-HS: Co<sub>3</sub>O<sub>4</sub> hollow spheres

CoO@N/S-CNF: CoO nanoparticles into nitrogen and sulfur co-doped carbon nanofiber networks

Co<sub>3</sub>O<sub>4</sub>/NRGO: Co<sub>3</sub>O<sub>4</sub>/N-doped reduced graphene oxide

C@Co-NGR: onion-like carbon@Co nanoparticles N doped graphene nanoribbons

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